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Thermochemistry of
Polybenzimidazole Foams

Utah Univ., Salt Lake City. Flammability
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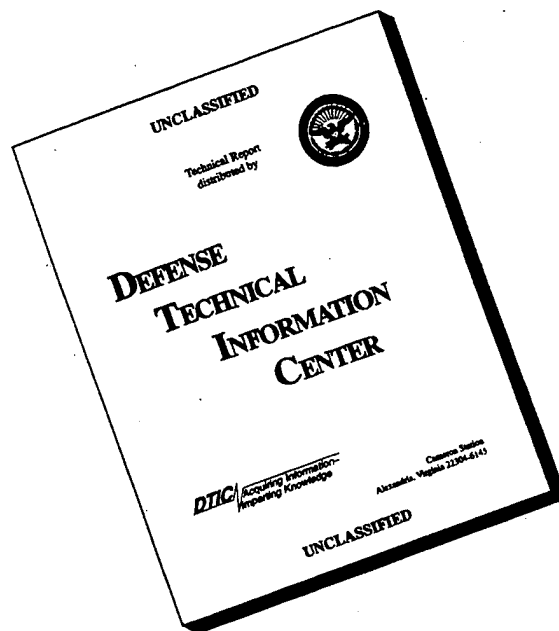
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THERMOCHEMISTRY OF POLYBENZIMIDAZOLE FOAMS

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ABSTRACT

As part of the National Aeronautics and Space Administration's program for the evaluation of the fire threat posed by exposure of space-age materials to various thermal and atmospheric environments, the Flammability Research Center at the University of Utah has carried out a detailed study of an aromatic polybenzimidazole (PBI) polymer. This study included an analysis of the low-boiling, high-boiling, and solid residue fractions resulting from the pyrolysis and nonflaming oxidative degradation of PBI polymer at temperatures up to 1000°C.

Both pyrolysis and nonflaming combustion were carried out in a thermoanalyzer, and the effluent gases were trapped on a porous polymer adsorbent. The degradation process was quenched at several intermediate temperatures, and the volatile products were analyzed using gas chromatographic-mass spectrometric techniques. The solid residues and the virgin polymer were characterized by elemental analysis, and the high-boiling fraction was investigated by chemical-ionization mass spectrometry (DVT452)

Any opinions, findings, conclusions or recommendations expressed in this publication are those of the author(s) and do not necessarily reflect the views of the National Science Foundation.

INTRODUCTION

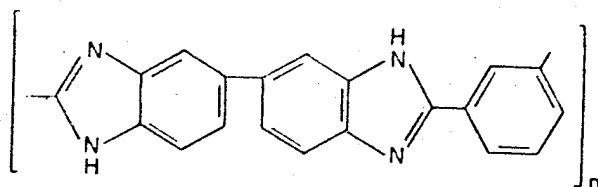
Considerable effort has been directed toward the development of space-age materials which might be used in the fabrication of aircraft interiors which are resistant to fire. To date the major concern of those engaged in the development of fire-retarded materials has been the reduction of the ignition tendency and a lowering of the material's flame propagation rate. Thus, it has been possible to meet existing code and regulatory requirements pertaining to these two material properties; but, in the opinion of the authors, the total physiological and toxicological hazard resulting from combustion processes has not been defined.

A fire-resistant aromatic polybenzimidazole (PBI) polymer developed to provide thermal insulation for aircraft fuselages was received from the Research and Development Division of the Whittaker Corporation. A program was designed to characterize this polymer and to identify the products of degradation resulting from pyrolysis, oxidative degradation, and flaming combustion.

Special emphasis was directed toward obtaining a complete material balance which would serve as the basis for future mechanistic studies pertaining to modes of polymer thermal decomposition. The qualitative and quantitative analysis of the products resulting from the material degradation serves as the basis of animal bioassay experiments designed to predict potential physiological and toxicological hazards to humans during fire exposure.

MATERIAL

The structure of the polybenzimidazole (PBI) foam used in this study was assumed to be



with a molecular weight per repeat unit of 308 gms. The foam samples were postcured at 450°C for 72 hours by the Whittaker Corporation before they were received by the Flammability Research Center.

EXPERIMENTAL PROCEDURES

Polymer Characterization

Samples of the PBI foams were ground to a #50 mesh size and dried at 100°C and 10^{-6} torr for several days. The ground polymer was stored in a dessicator; samples were removed from the dessicator prior to analysis.

Elemental Analysis

Carbon, hydrogen, and nitrogen analysis was performed on the PBI polymer using an F&M Model 185 C, H, and N Analyzer. Tests on compounds of known composition indicate that routine analyses are reliable to ± 0.5 percent for carbon and nitrogen and better than ± 0.3 percent for hydrogen. Identically dried samples of the polymer were sent to Schwarzkopf Microanalytical Laboratories (Woodside, New York) with instructions to dry the sample under vacuum prior to analysis. A summary of the results

from these analyses are presented in Table I along with the theoretical composition based upon the assumed structure of the repeat unit.

Infrared Analysis

In their recent study, Ehlers et al.¹ published the infrared spectra of several polybenzimidazoles. One compound discussed by these authors (labelled as Polymer IV), which was supplied to them by the Whittaker Corporation, had an infrared spectrum almost identical to that obtained in our laboratory using the KBr pellet technique. The only significant difference between the two spectra was the more intense O-H stretch in Polymer IV.

Ehlers et al.¹ also presented a spectrum of the pyrolyzate that was obtained by heating Polymer IV to 200°C. The spectrum of the pyrolyzate clearly showed a more pronounced N-H and a weakened O-H stretching band in comparison with the original polymer. Thus, the polymer studied herein had an infrared spectrum that closely matched the spectrum of the 200°C pyrolyzate of Polymer IV. This observation should not be surprising, since the PBI samples studied were subjected to the elevated temperature postcure treatment mentioned previously.

Thermoanalytical Studies

Experiments were conducted to determine the effect of the oxygen content in the samples' environment upon polymer degradation. Samples of the powdered PBI polymer, 10 ± 0.1 mg, were heated at 10°C/min from ambient to 1000°C in nitrogen, helium, and air environments. All gases used in the thermoanalyzer were checked for purity using gas chromatography (GC). A gas flow rate of 160 ± 10 ml/min was employed in all thermoanalyzer experiments.

TABLE I
ELEMENTAL ANALYSIS OF PBI POLYMER

Element	Percent Composition		
	Sample as Received		Theoretical ^b
	FRC Analysis	Commercial Laboratory Analysis ^a	
Carbon	77.7	77.7	77.9
Hydrogen	4.2	3.8	3.9
Nitrogen	18.1	18.1	18.2
Oxygen	0.0 ^c	0.0	0.0

^aResults from Schwarzkopf Microanalytical Laboratories

^bBased upon the structure of the repeat unit.

^cOxygen obtained by difference.

Figure 1 illustrates the thermogravimetric analysis (TGA) traces obtained from the experiments conducted in the air and nitrogen environments. The results obtained in a helium atmosphere were identical to those shown for nitrogen and thus are not reproduced here. An analysis of Figure 1 indicates that the polymer does not readily release loosely bound water, and further that there were no observable weight-loss changes below 375°C in the air environment. The samples exposed to an air environment began to decompose slowly at 375°C and degraded rapidly above 500°C. The sample in the air environment was entirely consumed at 670°C when heated at a rate of 10°C/min. The polymer samples subjected to heating in the inert environments were stable up to 550°C, after which they began to lose weight slowly. The heating was discontinued and the experiments terminated after a temperature of 1000°C was reached.

The effect of oxygen upon polymer degradation became evident when the differential thermal analysis (DTA) and derivative thermogravimetric analysis (DTG) traces illustrated in Figures 2 and 3 were examined. The DTA results indicated that the pyrolysis of the PBI polymer was slightly endothermic, whereas the nonflaming oxidative degradation process was exothermic and maximized at 570°C. The DTG thermograms also showed evidence of a maximum at 570°C in both nitrogen and air environments. The rate of sample weight loss was approximately six times greater during oxidative degradation than the rate measured during inert atmosphere pyrolysis.

The degradation process in nitrogen was clearly a bimodal process, with a second maximum occurring at 700°C. The first weight-loss process

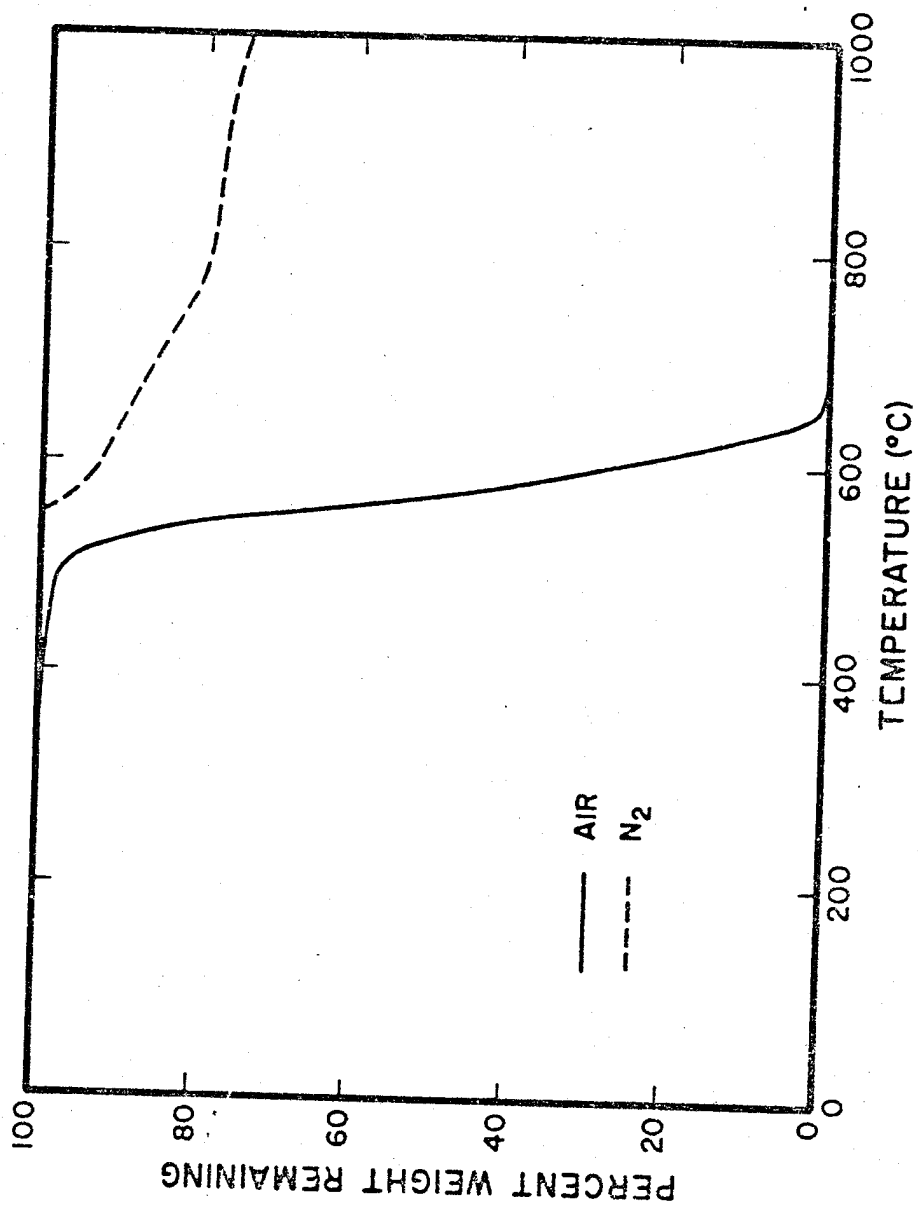


Figure 1. The effect of environment upon the degradation of PBI at a heating rate of 10°C/min.

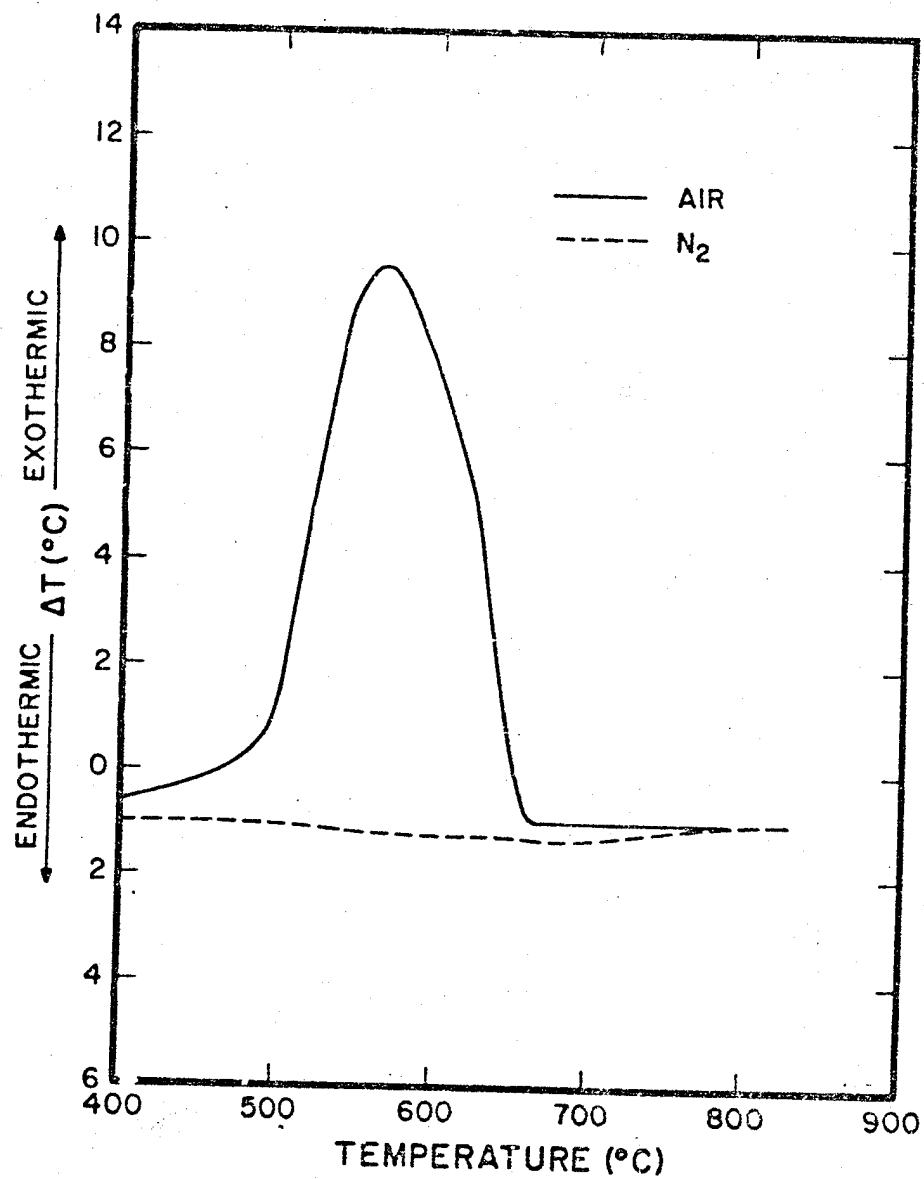


Figure 2. The DTA response for PBI in air and nitrogen environments.

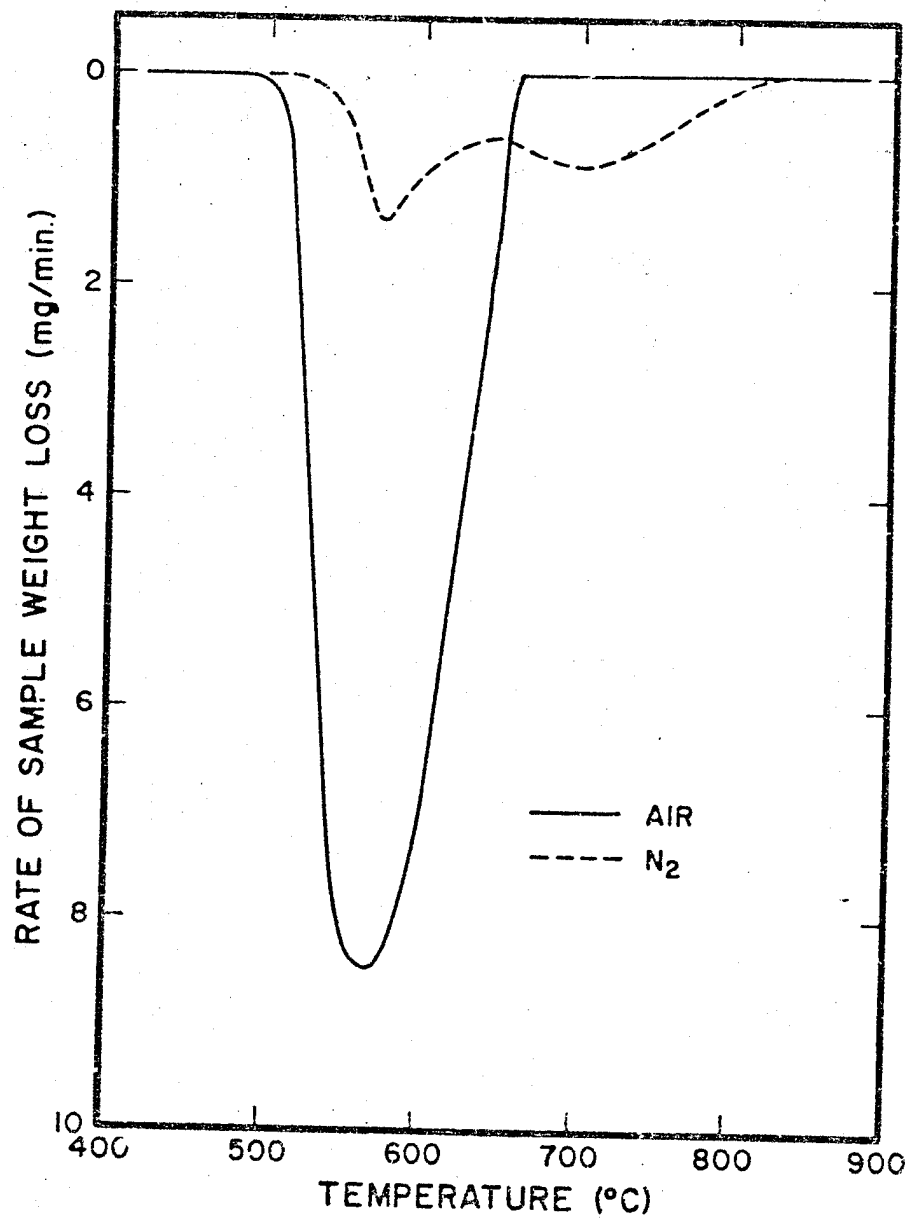


Figure 3. The DTG response for PBI in air and nitrogen environments.

in an inert environment, represented by the DTG maximum at 570°C, accounted for only three percent of the total sample weight. Such a small weight loss could be due to reactions of terminal end groups or loss of a light compound such as hydrogen, followed by further condensation of the aromatic polymer backbone. The second weight loss, beginning at 575°C and continuing up to 825°C, accounted for 23 percent of the initial polymer weight. This degradation step could also have involved a condensation process and may have resulted in extensive chemical rearrangement.

The analytical scheme used to identify the products resulting from polymer thermal degradation appears in Figure 4. An arbitrary division of the products into low-boiling volatiles, high-boiling volatiles, and solid residues has been made. Low-boiling volatiles are defined as those compounds which have significant vapor pressure under the conditions imposed by the apparatus used to desorb components (160°C); the high-boiling fraction consists of those species that condense at temperatures above 160°C and coat the inside surfaces of the reaction vessel and the associated gas transfer lines; and the solid residue is the material remaining in the sample holder.

Using the thermoanalyzer and procedures discussed in detail in a previous publication², samples of the PBI polymer were pyrolyzed in a nitrogen atmosphere at three different temperatures. The DTG results, shown in Figure 3, suggested that additional experiments were necessary to differentiate the degradation processes and to identify the products produced during each phase of the decomposition.

In this series of experiments, the polymer specimens were temperature-programmed from ambient to 570° at a heating rate of 100°C/min.

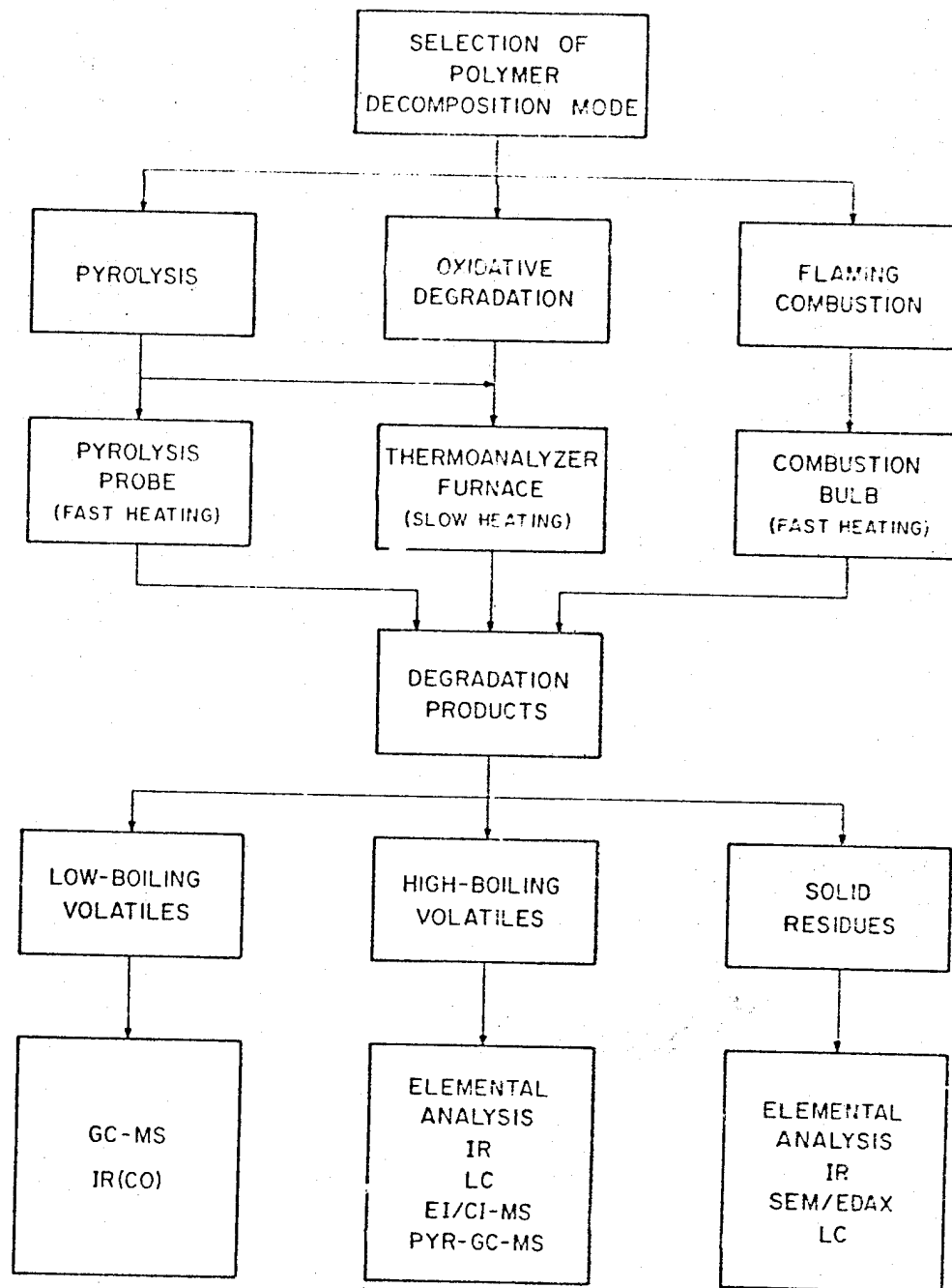


Figure 4. General analytical scheme.

Beginning at 300°C, the gaseous effluents were trapped for subsequent analysis. The products were sampled from the time the thermoanalyzer reached 300°C until four minutes after the furnace attained 570°C, at which time the heat source was removed and the reaction quenched. Following the analysis of the trapped volatile products, the furnace was again heated at a rate of 100°C/min up to a maximum of 700°C. Volatile gases were trapped beginning at 570°C, and the trapping was continued for four minutes after the furnace attained 700°C. The reaction was again quenched and then reheated at the same heating rate. In the third experiment the volatile products were collected between 700 and 1000°C and for a period of four minutes thereafter.

The collection of high-boiling fraction and samples of the solid residue could not be carried out during the above series of experiments because it would have necessitated disassembly of the furnace and contamination of the remaining sample with air. Therefore, samples of high-boiling volatiles that deposited on the glass-wool plug at the gas outlet on the furnace and the solid residue were collected in separate but identical experiments. The same sample temperature-programming procedure was used to insure consistency in the data. A third experiment was conducted to measure the carbon monoxide concentration as a function of temperature using the infrared absorption of the C-O stretch band at 2160 cm^{-1} .

The procedure described above was conducted four times for quantitation of the products that are described below. Additional experiments were performed using different trapping materials and GC column packings to help identify the volatile pyrolysis products. The results from the

analysis of low-boiling volatile products, high-boiling volatiles, and solid residues are presented in the following subsections.

Analysis of Volatiles--Pyrolysis Studies

The volatile products resulting from the pyrolysis of the PBI polymer were separated using a 3.2 meter long by 4 mm O.D. stainless-steel column containing Chromosorb 103 packing (Johns-Manville Co., Denver, Colorado). Additional experiments were conducted using a Chromosorb 101 GC packing on a column of the same dimensions. Thermal conductivity (TC) and flame ionization detection (FID) were used in these studies. A computerized Hewlett-Packard 5930 dodecapole mass spectrometer system was used for product separation and identification.^{2,3}

Table II contains a summary of the volatile products that have been identified and quantitated from these GC/MS experiments. A total of 15 compounds were identified as recorded and the amounts of each component that appeared at 300-570°C, 570-700°C, and 700-1000°C are listed in Table II. Experiments monitoring carbon monoxide evolution indicated that the sum of the CO produced from ambient to 1000°C did not exceed 0.1 mg/g of the polymer sample weight.

According to data presented in Table II, the PBI polymer sample initially lost 1.8 percent of the total sample weight in the form of water before sampling of the volatile products was begun. This water may be attributed to sample-moisture pickup during the experimental program. Between 300 and 570°C the sample weight loss, as measured by the TGA trace, amounted to 3.3 percent of the original sample weight; between 570 to 700°C and 700 to 1000°C, the sample weight losses were 13.2 and 10.8 percent, respectively.

TABLE II

SUMMARY OF THE VOLATILE PRODUCTS RESULTING FROM THE PYROLYSIS OF
PBI POLYMER IN NITROGEN AT THREE DIFFERENT TEMPERATURES^a

Compound	Peak ^b Number	T.E. ^c	R.F. ^d	Quantity (mg per gram of polymer) ^e		
				300 to 570°C	570 to 700°C	700 to 1000°C
Methane	3	0.05	0.450	3.5	30.	3.4
Nitrous oxide	5	1.00	0.890	0.84	0.69	5.5
Ehtylene	6	0.96	0.585	0.29	0.58	0.19
Acetylene	7	0.96*	0.59*	0.0	0.05	0.16
Ethane	8	0.96*	0.590	0.15	0.59	0.002
Cyanogen	9	0.99*	0.442*	0.012	0.0	0.0
Water	10	0.82	0.550	16.	34.	3.8
Propene	11	0.98*	0.652	0.23	12.	0.0
Hydrogen cyanide	12	0.99	0.442	0.35	43.	102.
Acetonitrile	14	0.95*	0.60*	0.0	1.7	0.22
Benzene	17	0.90	0.780	0.57	7.8	0.67
Toluene	18	0.95	0.794	0.29	1.3	0.26
Ethylbenzene	19	0.95	0.840	0.27	0.28	0.05
Benzonitrile	21	0.90*	0.895	0.0	10.4	0.0
Tolunitrile	22	0.90	0.895*	0 0	0.49	0.0
Totals				22.5	142.9	116.3

*Estimated

^aThe pyrolysis of three samples with an average weight of 21.6 mg.

^bCorresponds to peak numbers in the chromatograms.

^cRelative trapping efficiencies.

^dRelative response factors for a thermal conductivity detector..

^eSample lost an average of 3.3, 13.2, and 10.8 percent of the total sample weight during the pyrolysis from 300 to 570°C, 570 to 700°C, and 700 to 1000°C, respectively. Sample initially lost 0.39 mg, or 1.8 percent, of the sample weight in the form of water before sampling of effluents was begun at 300°C.

The material balance between the sum of volatile products and the actual weight loss from the samples of PBI polymer suggested that high-boiling volatiles may also have formed as the polymer degraded. The volatile compounds, listed in Table II (measured by thermogravimetric techniques), accounted for only 70 percent of the total sample weight loss which was observed between 300 and 570°C. The volatile products measured from the pyrolysis at higher temperatures accounted for the weight losses measured by the TGA to within experimental error.

Analysis of Solid Residues--Pyrolysis Studies

The solid residues that remained in the platinum crucible after exposure to the temperatures of 570°C, 700°C, and 1000°C in a nitrogen atmosphere were analyzed for carbon, hydrogen, and nitrogen content. Portions of the remaining polymeric material were removed from the crucible after the sample was heated under conditions similar to those in the experiments conducted to quantitate the volatile products. The nonvolatile residues formed in these experiments should be identical to the residues present after the low-boiling gases from the pyrolysis were analyzed. This data is necessary to determine the elemental composition of the residue and to obtain a material balance between the starting material and the products resulting from the pyrolysis experiments.

Table III contains a summary of the elemental analyses performed on the solid residues that formed at 570, 700, and 1000°C. For comparison, the elemental composition of the original sample is included in this table. Due to the hygroscopic nature of the sample, water absorption may account for the presence of trace amounts of oxygen shown in Table III. The composition of the solid residue at 570°C is nearly identical to the

TABLE III

ELEMENTAL ANALYSIS OF THE NONVOLATILE RESIDUES FORMED IN NITROGEN^a

Maximum Temperature (°C)	% Weight Remaining ^b	Percent Composition			
		Carbon	Hydrogen	Nitrogen	Oxygen ^c
Original Sample	100.0	77.7	4.2	18.1	0.0
570	94.0	79.2	3.5	16.8	0.5
700	80.8	84.5	1.3	11.7	2.5
1000	70.0	92.4	0.2	6.5	0.9

^aSamples heated at 100°C/min to the specified temperature.^bAs measured by TGA.^cDetermined by difference.

virgin material. At 700°C the residue had lost a substantial amount of hydrogen and nitrogen. This trend was also observed at 1000°C. The char that remained at 1000°C may have a structure similar to that of graphite. If it is assumed that the oxygen content results from bound water, the char structure may have an empirical formula of $C_{17}NH_{0.25}$.

Materials Balance--Pyrolysis Studies

A materials balance was calculated using the quantitative data for the volatile products listed in Table II and the composition of the solid residues listed in Table III. As shown in Table II, when the sample of PBI polymer was initially heated, there was a weight loss of 1.81 mg/g between ambient and 300°C as determined from the TGA. This weight loss was attributed to the loss of water.

Table IV includes an overall material balance between the virgin polymer and the sum of volatile products collected between ambient and 1000°C and the solid residue remaining at 1000°C. Out of the total sample weight loss of 296.5 mg/g, the volatile products account for 283 mg/g, or 95.4 percent, of the total observed weight loss. Virtually all (95 percent) of the carbon content lost from the sample was recovered in the form of volatile compounds, but the recoveries of hydrogen and nitrogen were only 60 and 66 percent, respectively. It should be noted that the volatile compounds were trapped on a porous polymer support at -112°C. Previous studies have shown that the light gases--carbon monoxide, methane, hydrogen, and nitrogen--are not effectively retained under these conditions.

TABLE IV

SUMMARY OF THE MATERIAL BALANCE FOR THE PYROLYSIS OF PBI POLYMER FROM
AMBIENT TO 1000°C

	Quantity in mg/g of Sample			
	Total Weight	Carbon	Hydrogen	Nitrogen
Original material ^a	1000.0	777.0	42.0	171.0
Solid residue	699.8	646.6	1.4	45.5
Sample weight loss	296.5	130.4	40.6	125.5
Volatiles recovered	282.9	124.3	24.6	82.9
Percentage of volatiles recovered	95.4	95.3	60.6	66.0
Percentage of total sample accountable	98.3	99.2	61.9	75.1

^aElemental composition based upon analysis of virgin polymer.

Using these analytical results, one can draw some conclusions about the process of PBI polymer degradation as a function of sample temperature. Below 300°C the sample did not undergo any visible changes in color or integrity. The only weight change was attributable to the loss of loosely bound water. Above 570°C the sample began to lose weight ~~more~~ rapidly as the degradation process accelerated. Figure 5 depicts the concentrations of the major volatile components which were analytically determined at 570, 700, and 1000°C. As this figure illustrates, the major weight losses at 570°C were in the form of water and methane. The elemental analysis of the solid residue at 570°C indicated that 20 percent of the hydrogen content of the virgin material was lost during this heating period; hence, it is reasonable that a hydrogen-rich compound such as methane was observed to be a major product. Hydrogen gas could possibly be another product of the early stages of polymer degradation. The loss of methane and perhaps hydrogen gas would necessitate the formation of a more condensed heterocyclic structure for the remaining sample. A major portion of the sample weight loss was attributed to the formation of a relatively non-volatile material, perhaps oligomeric fragments, from the polymer.

Between 570 and 700°C there was a dramatic increase in the formation of aromatic and unsaturated compounds including propene, acetonitrile, benzene, and benzonitrile. The solid residue had lost approximately 70 percent of the original hydrogen content at 700°C through the formation of a substantial quantity of methane. As shown in Figure 5, hydrogen cyanide, water, and methane are the most abundant products at this stage of polymer degradation. If any high-boiling volatiles were being formed in the decomposition process, they were most likely thermally degraded to a more

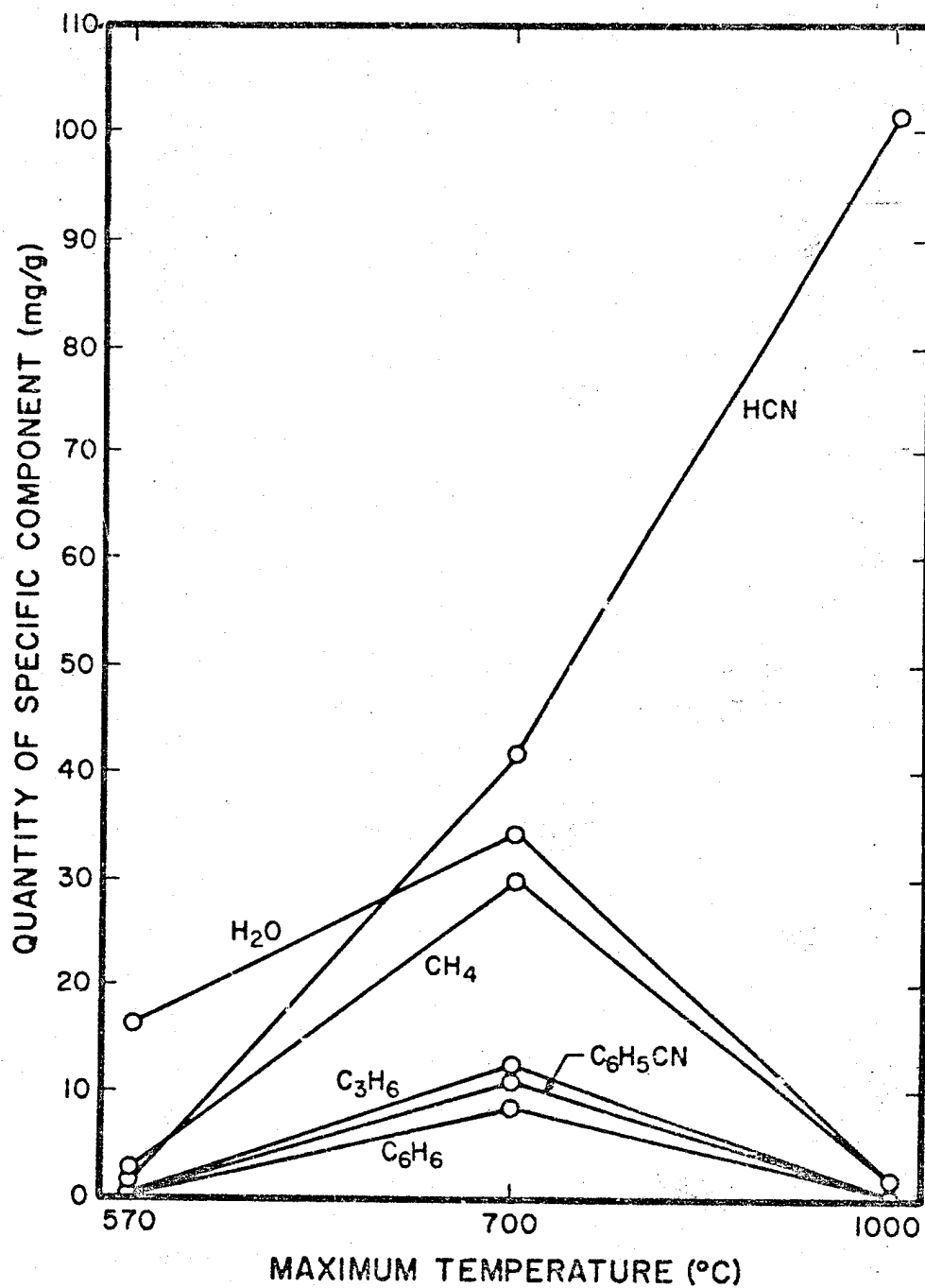


Figure 5. Observed concentrations of major volatile products from the pyrolysis of PBI polymer at three temperatures.

volatile, low molecular-weight species before escaping from the furnace.

Above 700°C, the shift in volatile products was decidedly toward more hydrogen-deficient species. At 1000°C, virtually none of the hydrogen and 38 percent of the nitrogen remained in the char, which now possessed a graphite-like character. Hydrogen cyanide was by far the dominant volatile product of the thermal degradation process above 700°C.

Analysis of Volatiles--Oxidative Degradation Studies

Oxidative degradation studies were conducted in the thermoanalyzer using an air environment from ambient to approximately 900°C, at which point no solid residue remained. The volatile products were zone trapped in two regions: ambient to 570°C and 570 to 900°C. The same methods of trapping, separation, and identification were used as those discussed previously.

A summary of the volatile products resulting from oxidative degradation is shown in Table V. A total of 11 compounds were identified and quantitated from these experiments, and the amounts of each component are listed in mg per gram of original polymer sample. Prior to sampling of the volatile products, the polymeric material lost approximately two percent of the total sample weight, presumably in the form of loosely bound water. During the sampling period between 300 and 570°C, the PBI polymer lost approximately 24.4 percent of its original sample weight, according to the TGA trace.

This corresponds to 453 percent of the sample weight loss as indicated by the TGA curve. Virtually all the volatile products were in the form of nitrogen. A comparison of the volatile products resulting

TABLE V

SUMMARY OF THE VOLATILE PRODUCTS RESULTING FROM THE OXIDATIVE DEGRADATION
PBI POLYMER IN AIR AT TWO DIFFERENT TEMPERATURES^a

Compound	Peak Number ^b	T.E. ^c	R.F. ^d	Quantity ^e	
				Ambient to 570°C ^f	570 to 900°C ^g
Carbon monoxide	--	--	--	4.9	16.4
Nitric oxide	2	1.00	0.820	2.4	2.2
Carbon dioxide	4	0.97	0.915	944.	2285.
Nitrous oxide	5	1.00	0.890	4.6	5.5
Cyanogen	9	0.99*	0.600	0.08	0.18
Water	10	0.82	0.550	149.	149.
Hydrogen cyanide	12	0.99	0.600	0.24	0.25
Acetonitrile	14	0.95*	0.60*	0.71	0.51
Benzene	17	0.90	0.780	0.10	0.07
Toluene	18	0.95	0.794	0.022	0.023
Ethylbenzene	19	0.95	0.840	0.025	0.0
Totals				1106.1	2459.1

*Estimated.

^aThe degradation of two samples with an average weight of 9.9 mg.

^bCorresponds to peak numbers in the chromatograms.

^cRelative trapping efficiencies.

^dRelative response factors for a thermal conductivity detector.

^eMilligrams of compound produced per gram of polymer as measured by analytical techniques.

^fPolymer specimen lost 24.4 percent of the total sample weight during experiment as determined by the TGA.

^gPolymer specimen lost 75.6 percent of the total sample weight during experiment as determined by the TGA.

^hQuantity determined by spectroscopic techniques. See text for details.

from the oxidative degradation of the PBI polymer (Table III) clearly indicates that oxygen in the sample's environment has reacted with the polymer during heating to give rise to these oxygen-containing compounds. Similar observations were noted for the decomposition occurring between 570 and 900°C.

Materials Balance--Oxidative Degradation

The quantitative data presented in Table V for the low-boiling volatiles produced from the oxidative degradation of PBI polymer allows one to calculate a material balance for the experiments reported herein. The results of these calculations are shown in Table VI. The task of obtaining a material balance is greatly simplified by the knowledge that all the virgin polymer was volatilized by 900°C in the oxidative degradation process. However, since the composition of the solid residue was not determined at 570°C, one cannot estimate the material recovery at this intermediate temperature.

From the data presented in Table V, 1106 mg/g of volatile products were recovered from the oxidative degradation reaction between ambient and 570°C. Seventy-three percent of the total weight of volatile products formed between 570 and 900°C was in the form of oxygen present in carbon monoxide, nitric oxide, carbon dioxide, nitrous oxide, and water.

The data in Table VI summarize the mass balance data for PBI polymer degraded in an air environment. The recovery of the carbon content contained in the original polymer was quantitative (108.0 percent) hydrogen was slightly low (85.7 percent), and only a limited amount of nitrogen was actually recovered (5.6 percent). If one were to totally combust PBI polymer, the products of the reaction would be carbon dioxide,

TABLE VI
MATERIALS BALANCE FOR THE OXIDATIVE DEGRADATION
OF PBI POLYMER IN AIR AT 570 AND 900°C

Temperature Range	Quantity in mg/g of Sample				
	Total Weight	Carbon	Hydrogen	Nitrogen	Oxygen
27°C (original material) ^a	1000	777.0	42.0	181.0	0
27 to 570°C:					
Volatiles recovered	1106	237.0	17.7	4.6	847
570 to 900°C:					
Volatiles recovered	2759	602.0	18.3	5.5	1804
Total, 27 to 900°C					
Sample weight loss	1000	777.0	42.0	181.0	0
Volatiles recovered	3565	839.0	36.0	10.1	2641
Percentage recovered	--	108.0	85.7	5.6	--

^aElemental composition based upon analysis of virgin sample.

water, and nitrogen gas. Thus, since the conditions in the thermoanalyzer approach an environment that can supply sufficient oxygen to the sample specimen to totally combust the sample, it is not unreasonable to postulate that N_2 was a major degradation product. Since the analytical procedure employed in these experiments was quantitative for oxides of nitrogen, amines, nitriles, and ammonia, there seems to be no alternate explanation for the low recovery of nitrogen than the formation of N_2 . Experiments are currently underway to quantitate the amount of nitrogen gas evolved in the oxidative degradation of PBI polymer.

SUMMARY

A summary of the volatile products formed during the pyrolysis and oxidative degradation of PBI polymer specimens are presented in Table VII. Many of the saturated and unsaturated hydrocarbons formed during the pyrolysis experiments were not observed during decomposition in the oxygen-containing environment. This change in product distribution is attributable to either a change in the overall polymer degradation mechanism and/or the possibility that the hydrocarbons were acting as a fuel source once they were volatilized. Since the DTA curves for the polymer degradation in nitrogen and in air (Figure 2) were decidedly different, one can conclude that oxygen was reacting with the polymeric sample while in the solid state. One cannot discount the possibility that some fraction of hydrocarbon products was formed in the oxidative environment via the same mechanism as that which occurred in the pyrolysis of PBI polymer. The temperature of the first maximum DTG responses (Figure 3) were coincident, but the onset temperatures of degradation (Figure 1) differed by more than 150°C.

Because of the excellent thermal stability exhibited by polybenzimidazoles, numerous laboratories have studied the pyrolysis products of materials with structures related to the PBI used in this study. Shulman and Lochte⁴ studied polymers possessing similar structures that had been subjected to several different postcuring treatments. The pyrolysis products were monitored by mass spectroscopy to 950°C and the solid residues were examined for their elemental analysis. Although water was the only significant product identified below 550°C, the major volatile

TABLE VII
A SUMMARY OF THE PRODUCTS FROM PYROLYSIS AND
OXIDATIVE DEGRADATION OF PBI POLYMERS

Compound	Quantity (mg/g)				
	Pyrolysis			Oxidative Degradation	
	300-570°C	570-700°C	700-1000°C	27-570°C	570-900°C
Carbon monoxide	0.0	0.0	0.0	4.9	16.4
Carbon dioxide	0.0	0.0	0.0	867.	2152.
Nitric oxide	0.0	0.0	0.0	2.4	2.2
Nitrous oxide	0.84	0.69	5.5	4.6	5.5
Water	16.	34.	3.8	149.	149.
Hydrogen cyanide	0.35	43.	102.	0.24	0.25
Cyanogen	0.012	0.0	0.0	0.08	0.18
Methane	3.5	30.	3.4	0.0	0.0
Ethane	0.15	0.59	0.002	0.0	0.0
Ethylene	0.29	0.58	0.19	0.0	0.0
Acetylene	0.0	0.05	0.16	0.0	0.0
Propene	0.23	12.	0.0	0.0	0.0
Acetonitrile	0.0	1.7	0.22	0.71	0.51
Benzene	0.57	7.8	0.67	0.10	0.07
Toluene	0.29	1.3	0.26	0.02	0.02
Ethylbenzene	0.27	0.28	0.05	0.025	0.0
Benzonitrile	0.0	10.4	0.0	0.0	0.0
Tolunitrile	0.0	0.49	0.0	0.0	0.0

products above this temperature were H_2 , CO , CO_2 , CH_4 , H_2O , HCN , and NH_3 . The authors postulated that water was present, even in well-cured samples, and most likely reacted at elevated temperatures with the condensed polymer structure to form a hydroxyimidazole intermediate. The intermediate was believed to readily decompose to form hydrogen cyanide and a highly condensed nitrogen-containing heterocyclic residue.

Friedman, Goldstein, and Griffith⁵ studied several polybenzimidazoles in vacuum up to $1000^\circ C$. These authors observed higher molecular weight products as well as the lighter gases reported by Shulman and Lochte⁴, including acrylonitrile, phthalonitrile, benzene, aniline, and benzonitrile. Friedman et al.⁵ concluded by suggesting that the observed product distribution is profoundly altered by the specific method of sample preparation and the apparatus used for pyrolysis.

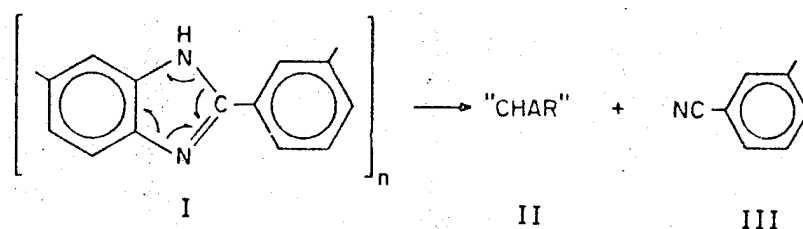
A series of 10 polybenzimidazole derivatives were examined in a more recent report by Ehlers, Fisch, and Powell.¹ These authors studied the pyrolysis of several materials to $650^\circ C$ which had an assumed structure that was the same as the PBI samples reported here. However, the elemental analysis of the polymers studied by Ehlers et al. contained several percent oxygen which, it was believed, resulted from phenoxy-end groups and incomplete polymerization. One polymer, signified as Polymer I, had a composition that closely matched the elemental analysis of the PBI samples studied here. The data reported for the elemental composition of the virgin polymer and the solid residues at 550 and $650^\circ C$ from Polymer I are compared to results from this report in Table VIII. Although different heating rates and maximum pyrolysis temperatures were used in these two studies, both sets of data indicate a similar rise in the percentage of carbon and the concurrent lowering of the hydrogen and nitrogen content in the solid residue.

TABLE VIII

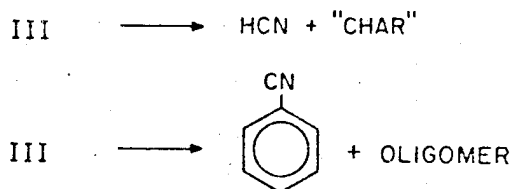
COMPARISON OF ELEMENTAL ANALYSIS OF POLYMER AND NONVOLATILE RESIDUES WITH DATA FROM LITERATURE

Sample	Temperature (°C)	% Weight Remaining	Percent Composition			
			Carbon	Hydrogen	Nitrogen	Oxygen
Ehlers et al. ¹	23	100.0	76.2	4.1	17.3	2.6
	550	88.5	76.9	3.4	15.2	3.4
	650	81.8	82.6	1.6	13.6	2.4
This study	23	100.0	77.7	4.2	17.1	1.0
	570	94.0	79.2	3.5	16.8	0.5
	700	80.8	84.5	1.3	11.7	2.5

The major degradation products from Polymer I at 550°C were H₂, CH₄, HCN, CO, NH₃, and benzene. At 650°C, the major gaseous products were H₂, HCN, CH₄, and CO. In the overall degradation process from 27 to 650°C, hydrogen cyanide was the most abundant volatile product by weight. In the analysis reported here, the major degradation products at 700°C were H₂O, HCN, CH₄, propene, benzene, and benzonitrile. These data most easily fit the degradation mechanism proposed by Ehlers et al. which involves the thermolytic cleavage of a C-N bond:



Structure III can further react to form either benzonitrile or hydrogen cyanide:



The formation of methane and propene most likely results from the cleavage of the aromatic rings in the polymer backbone. Since no volatile amines or nitrogen heterocyclic compounds were observed as products, it is likely that structures such as II undergo free-radical reactions and form condensates. This phenomena has also been proposed in the degradation of aromatic polyimide polymers to explain the lack of nitrogen-containing volatile compounds and nonvolatile residues possessing a high nitrogen content⁶.

Recently, a study on a series of polybenzimidazole polymers was reported by Tsur, Freilich, and Levy⁷. Volatile products were monitored using mass spectrometric techniques by directly sampling effluents from a thermogravimetric analyzer up to temperatures of 800°C. These authors reported that the gaseous composition of the pyrolysis products from polybenzimidazoles roughly corresponds to the data reported by Shulman and Lochte⁴ except for the presence of ammonia. Since these authors monitored the NH_3 concentration by observing the intensity of the m/e 17 (NH_3^+) ion, there is some uncertainty in the data due to an interference by the OH^+ ion from water. Tsur et al.⁷ were unable to monitor the presence of other gaseous products when exposed to air because of interferences with gases that are present in air.

In conclusion, the results presented herein for PBI polymer are generally in agreement with reports in the literature on related polymeric materials. However, unlike most other polybenzimidazoles that have been studied, the PBI material supplied by the Whittaker Corporation contains very little oxygen, other than in the form of water, in the polymeric structure. As a consequence, a majority of oxygen-containing compounds reported by others were not detected in this study. Unlike some reports in the literature, ammonia was not a major pyrolysis product. The major volatile product, hydrogen cyanide, is most likely formed in a thermal cleavage of the imidazole linkage.

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